

## The effect of soil acidity on potentially mobile phosphorus in a grassland soil

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(Revised MS received 16 May 2002)

### SUMMARY

This study compared phosphorus (P) speciation and the relationship between bicarbonate extractable (Olsen) P and 0.01 M CaCl<sub>2</sub> extractable P (a measure of potentially mobile P) in soils from plots of the Park Grass experiment started in 1856 at IACR-Rothamsted, UK and with and without nitrogen as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and with and without calcium carbonate (CaCO<sub>3</sub>, lime). A point, termed the change point, was noted in Olsen P, above which 0.01 M CaCl<sub>2</sub>-P increased at a greater rate per unit increase in Olsen P than below this point. Previous findings have shown a change point for soils with a pH > 5.8 at 56 mg Olsen P/kg and at 120 mg Olsen P/kg for soils below this pH. Soils given (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> annually since 1856 and with lime periodically since 1903 mostly had a pH between 3.7 to 5.7, some of these (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> treated soils were limed to pH 6.5 and above from 1965. Irrespective of their pH in 1991/92 all the soils had a similar change point (120 mg Olsen P/kg) to that found for other soils with pH < 5.8 (112 mg Olsen P/kg). In a laboratory study lasting 30 days, the addition of CaCO<sub>3</sub> to acid soils from the field experiment that had received (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> had a similar change point to soils with pH < 5.8 irrespective of pH, suggesting soil P chemistry was controlled by the long period of soil acidity and this was not reversed by a short period at a higher pH. The effect of pH was attributed to the creation of P sorptive surfaces on aluminium precipitates compared with less acidic soils (pH > 5.8) where there was less exchangeable Al to be precipitated. This was confirmed with solid-state <sup>31</sup>P nuclear magnetic resonance, which indicated that for soils of similar total P concentration and pH, there was twice as much amorphous Al-P in soils given (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> compared with those without. Changes in pH as a result of applications of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or lime can greatly change the concentration of potentially mobile P due to the effects on Al solubility. Although there was less potentially mobile P in soils with pH < 5.8 than in soils above this pH, it is usually advised in temperate regions to maintain soils about pH 6.5 for arable crops.

### INTRODUCTION

Phosphorus (P) concentration in overland flow and subsurface drainage waters is related to soil P concentration (McDowell & Sharpley 2001). Molybdate reactive P (MRP) in 0.01 M CaCl<sub>2</sub> extracts (CaCl<sub>2</sub>-P) has a similar relationship with Olsen P as has dissolved reactive P (DRP) in overland flow or subsurface drainage waters. The relationship between CaCl<sub>2</sub>-P or DRP (intensity, I) and Olsen P (quantity, Q) in drainage waters exhibits a point, termed a change point, above which CaCl<sub>2</sub>-P increases at a much greater rate than below (Hesketh & Brookes 2000). McDowell *et al.* (2001) showed that the Q/I relationships of several soils including soils from

treatments of the Park Grass experiment (IACR-Rothamsted, UK) were affected by pH. Contradictory evidence exists to show that liming can both increase and decrease the concentration of exchangeable P and P in soil solution (Holford 1983; Biswas & Tomar 1997). Our aim was to examine, on one soil type, the effect of soil pH on the potential mobility of P using soils from the Park Grass experiment.

### MATERIALS AND METHODS

#### Soils

Air-dried, crushed and sieved (< 2 mm) soil samples from either the 0–7.5 cm or 0–23 cm depth, taken in

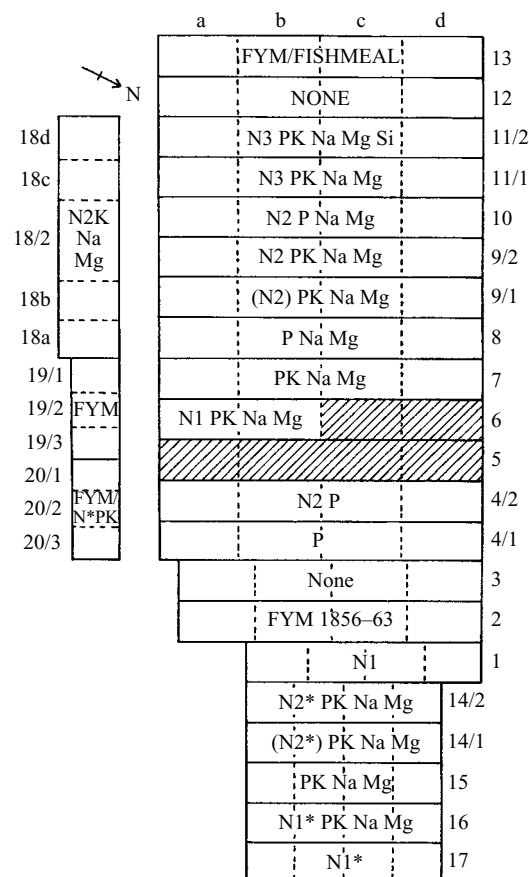


Fig. 1. Plan of the Park Grass experiment. Mineral fertilizers (applied in winter, except N applied in spring)

N1, N2, N3 ammonium sulphate supplying 48, 96, 144 kg/ha N respectively  
 N1\*, N2\* sodium nitrate supplying 48, 96 kg/ha N respectively  
 P 35 kg/ha P as superphosphate  
 K 225 kg/ha K as sulphate of potash  
 Na 15 kg/ha Na as sulphate of soda  
 Mg 10 kg/ha Mg as sulphate of magnesia  
 Si 450 kg/ha of silicate of soda

Organics (applied every fourth year)  
 FYM 35 t/ha<sup>-1</sup> fresh farmyard manure (bullocks over-wintered on straw bedding in covered yards)  
 Fish-meal to supply 63 kg N/ha  
 Lime as needed to maintain pH 7, 6 and 5, respectively since 1965  
 d unlimed

1992 from the Park Grass experiment (Fig. 1) were used in this study. The soil is a silty clay loam of the Batcombe Series (Stagnogleyic paleo-argillic brown earth classified as a Chromic Luvisol; FAO 1990).

The 20 original plots have received various quantities of mineral fertilizer, including P, potassium (K) and nitrogen (N) as either  $\text{NaNO}_3$  or  $(\text{NH}_4)_2\text{SO}_4$ , and organic manures at different periods since 1856. At the beginning of the Park Grass experiment in 1856 there is good evidence to suggest that soil pH was 5.7–5.8 (Johnston *et al.* 1986). There have been only small changes in soil pH (about 1 unit) on plots that have received N as  $\text{NaNO}_3$ , FYM or no N and no lime. However, some treatments that have received N as  $(\text{NH}_4)_2\text{SO}_4$  annually, again with no lime, now have a pH as low as 3.7 (Johnston *et al.* 1986). Applying lime once every 4 years to one half of each plot began in 1903. In 1964, limed and unlimed half plots were each halved again to make four subplots, *a*, *b*, *c* and *d*, one to remain unlimed (*d*) and the other three to receive lime calculated to establish and maintain a pH of 5 (*c*), 6 (*b*) and 7 (*a*) (Warren *et al.* 1965).

### Analyses

Soils from all subplots of treatments that had received  $(\text{NH}_4)_2\text{SO}_4$  and *d* subplots from three other treatments were analysed for Olsen P (Olsen *et al.* 1954; soil to 0.5 M  $\text{NaHCO}_3$  ratio, 1:20) and 0.01 M  $\text{CaCl}_2$ -P ( $\text{CaCl}_2$ -P; Scholfield 1955; soil to solution ratio, 1:5). In each case the shaking time was 30 min. Scholfield (1955) and Scholfield & Taylor (1955) chose to measure soil pH and readily soluble P in 0.01 M  $\text{CaCl}_2$  because the ionic concentration was similar to that in the soil solution, where soil pH exceeded 6.5 and the dominant cation was Ca. For consistency, the same Ca concentration was used to analyse all soils used in our experiments. The sampling depth for *d* subplots was 0–23 cm and 0–7.5 cm for the *a*, *b* and *c* subplots. Soil pH was determined in water (soil to solution ratio of 1:2.5), and organic carbon (C) by the method of Grewal *et al.* (1991). Additional Olsen P,  $\text{CaCl}_2$ -P and total P data for soils with pH > 5.8 (mostly *a* and *b* subplots) are taken from McDowell & Condron (1999).

To estimate the solubility of soil P minerals in 0.01 M  $\text{CaCl}_2$ , ion activity products (IAP) were determined from chemical activities generated from ion concentrations in solution, calculated using the MINTEQA2 chemical speciation model and compared with published solubility products for P minerals in their standard state (Allison *et al.* 1991). Duplicate samples of each soil (5 g, < 2 mm air-dried) were suspended in 25 ml of 0.01 M  $\text{CaCl}_2$  (to provide an equilibration matrix of fixed ionic strength). After shaking for 16 h the pH was determined using a glass electrode with a reference electrode in 0.01 M  $\text{CaCl}_2$ . The suspensions were centrifuged for 30 min at 4000 rpm and filtered through a 0.45  $\mu\text{m}$  membrane. Nitrate, sulphate, fluoride and chloride were measured using a Dionex ion chromatograph (Dionex, Sunny-

Table 1.  $^{31}\text{P}$  high power decoupling magic angle spinning nuclear magnetic resonance peak assignments (chemical shift) used to define the sum total of Al-P and Ca-P species

Peak	Chemical shift (ppm)	Mineral
Al-P species		
1	-25†	Berlinite [ $\text{AlPO}_4$ ]
2	-19†	Variscite [ $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ]
3	-13 to -11‡§	Wavellite [ $\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ ]
4	-7‡	Al-P
Ca-P species		
5	-2§	Monetite [ $\text{CaHPO}_4$ ]
6	3§	Hydroxyapatite [ $\text{HA}$ : $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ], octocalcium phosphate [ $\text{OCP}$ : $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ ] and/or amorphous calcium phosphate
7	9	Dicalcium phosphate dihydrate [ $\text{DCPD}$ : $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ]

† Bleam *et al.* (1989); ‡ Lookman *et al.* (1996); § Frossard *et al.* (1994); || Rothwell *et al.* (1980).

vale, CA). Molybdate reactive P was measured colorimetrically (Murphy & Riley 1962). Magnesium (Mg), aluminium (Al), and iron (Fe) were determined using atomic absorption spectroscopy (AAS). Calcium (Ca) was also measured by AAS and the data confirmed that no Ca had exchanged in any of the

soils. Sodium (Na) and potassium (K) were determined by flame photometry and ionic strength estimated from electrical conductivity (Griffin & Jurinak 1973).

Solid-state  $^{31}\text{P}$  HPDec/MAS NMR spectra were obtained using a Bruker MSL 300 operating at 121.5 MHz for  $^{31}\text{P}$ . Soil samples (< 150  $\mu\text{m}$ ) were packed into 4 mm zirconia rotors, with Kel-F caps and spun at magic angle spinning rates of 6.5 to 10 kHz. A repetition rate of 500 ms was used. Depending upon the sample, between 43000 and 105000 scans were accumulated (6 to 15 h). Chemical shifts ( $\delta$  ppm) were determined relative to 85% orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ). Individual peaks for Al- and Ca-associated P species (see Table 1) were assigned using the Winfit program. To make data semi-quantitative an acid ammonium oxalate extraction (McKeague & Day 1966) was used as a reference to quantify the molar concentrations of Al, Fe and P in the soils and Al, Fe and Ca associated P in  $^{31}\text{P}$  HPDec/MAS NMR spectral fits (Lookman *et al.* 1996; McDowell *et al.* 2002).

Table 2. General characteristics of soils (0–23 cm) used for the laboratory liming study

Subplot	pH	Organic C (g/kg)	Olsen P* (mg/kg)	$\text{CaCl}_2\text{-P}$ (mg/l)
4/2d	3.7	45	213	2.5
9/2d	3.6	42	186	0.8
11/1d	3.5	45	112	0.9
13d	4.7	50	34	0.4
15d	4.8	42	151	2.6
16d	5.3	49	94	2.0

\* Differences in Olsen P reflect differences in the P balance on the plots since 1856.

Table 3. Mean and range (w) of soil characteristics at 0–7.5 and 0–23 cm depths for  $(\text{NH}_4)_2\text{SO}_4$  treated plots compared with all other plots with pH > and < 5.8

Parameter	$(\text{NH}_4)_2\text{SO}_4$ fertilized soils		All other soils < pH 5.8		All other soils > pH 5.8
	0–7.5 cm	0–23 cm	0–7.5 cm	0–23 cm	0–7.5 cm
pH	5 (0.2)	3.7 (0.3)	4.5 (0.2)	4.7 (0.1)	6.2 (0.1)
w	3.7–6.4	3.5–4.3	4.1–5.0	4.1–5.7	5.8–6.7
Organic C (g/kg)	72 (8)	26 (1)	44 (2)	33 (3)	54 (4)
w	49–122	23–28	40–50	21–49	31–79
Olsen P (mg/kg)	154 (4.9)	130 (46.0)	88 (21.0)	67 (15.6)	68 (7.9)
w	130–201	31–213	13–152	11–167	4–125
$\text{CaCl}_2\text{-P}$ (mg/l)	0.9 (0.12)	0.2 (0.09)	0.5 (0.18)	1.1 (0.16)	1.9 (0.26)
w	0.4–2.7	0.1–0.5	0.1–1.1	0.2–4.0	0.2–5.9

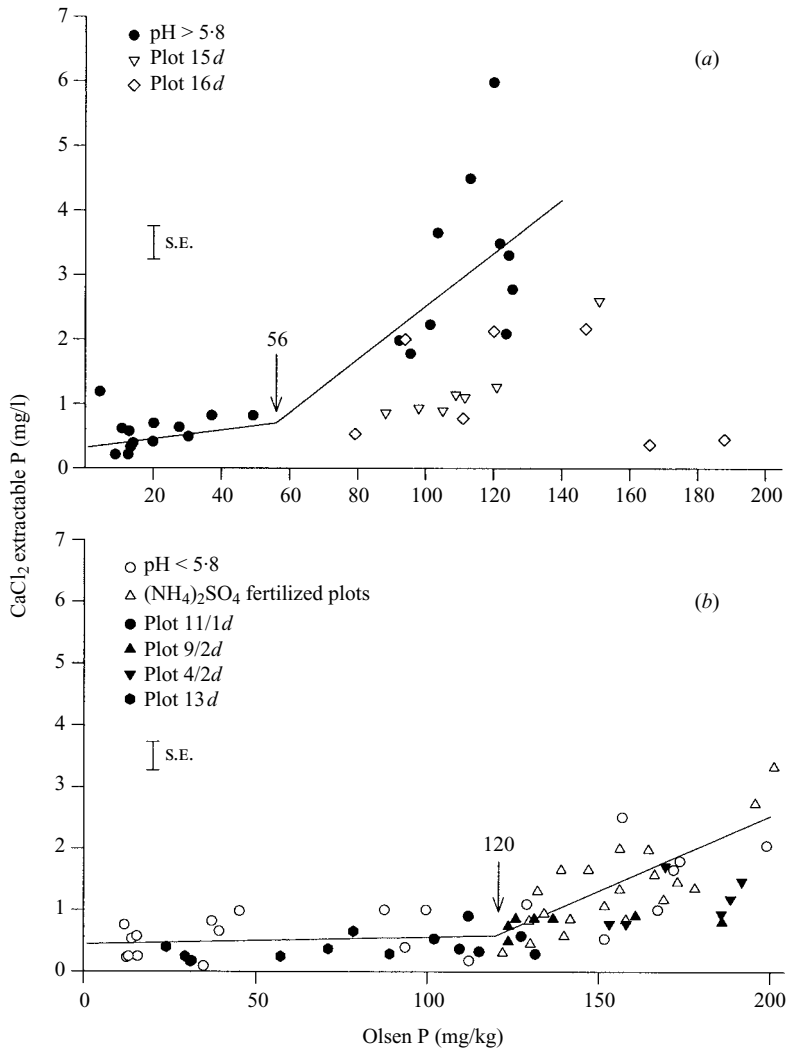


Fig. 2.  $\text{CaCl}_2$ -P against Olsen P for soils above and below pH 5.8 and soils receiving N as  $(\text{NH}_4)_2\text{SO}_4$ . Note: in (a) open symbols are data from the laboratory liming experiment and in (b) closed symbols are data from the laboratory liming experiment.

#### Laboratory liming experiment

Soils, 0–23 cm, from *d* subplots that had not received lime were taken from the following six plots: 13*d* (organic manures), 15*d* (PK only) and 16*d* (PK plus  $\text{NaNO}_3$ ) and three plots, all of which had  $(\text{NH}_4)_2\text{SO}_4$  namely 4/2*d* (P), 9/2*d* (PK) and 11/1*d* (PK) (Table 2). Seven samples of each soil (50 g) were weighed out and to six of them reagent grade  $\text{CaCO}_3$ , calculated to give a range of pH up to 8 (Rowell 1994), was added and mixed well. The soils were wetted and maintained at 60% field capacity and incubated open to the air at 25 °C for 30 days. Following incubation, each soil was analysed for Olsen P,  $\text{CaCl}_2$ -P and pH in water.

#### Statistical analyses

Most statistical analyses were conducted with SPSS (SPSS Inc, 1999) including means and standard errors. The  $\text{CaCl}_2$ -P versus Olsen P data were fitted to a split line model (McDowell & Sharpley 2001) using Genstat v5 (Genstat 5 Committee 1995).

## RESULTS AND DISCUSSION

#### Data for soils from the field experiment

Soils used in this study had a wide range of values for pH, organic carbon, Olsen P and  $\text{CaCl}_2$ -P (Table 3) as

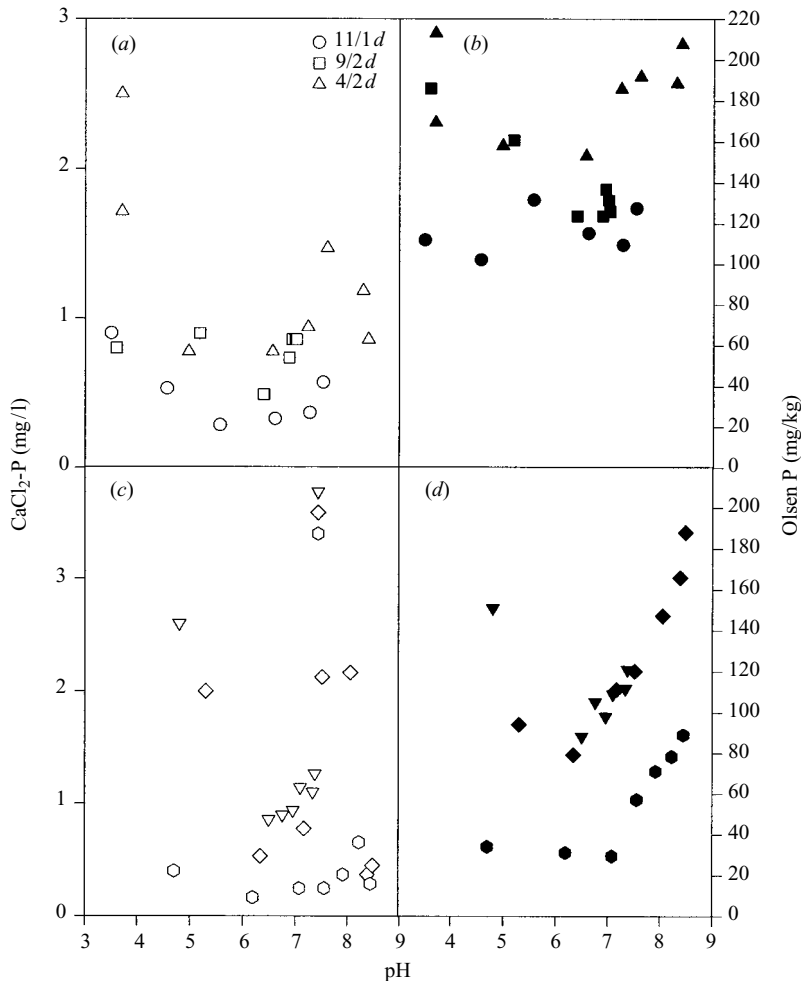


Fig. 3. The relationship between CaCl<sub>2</sub>-P (open symbols) and Olsen P (closed symbols) and soil pH following the liming of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> fertilized soils (*a* and *b*) and soils that had not received any (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (*c* and *d*) in the laboratory liming experiment.

a result of their past history of nutrient additions and liming. Thus, it is possible to test the relationship between Olsen P and CaCl<sub>2</sub>-P over a wide range of values and assess the effects of pH and organic carbon on the relationship.

A plot of CaCl<sub>2</sub>-P against Olsen P for soils with pH > 5.8 is shown in Fig. 2*a*. The change point, estimated by fitting two straight lines (McDowell & Sharpley 2001) occurs at 56 mg Olsen P/kg. This value is very similar to that for soils of similar pH from the Barnfield experiment but somewhat larger than that of the Broadbalk experiment, both at Rothamsted (McDowell *et al.* 2001). All three soils have a similar texture but the Park Grass soil (0–23 cm) contains about three times more soil organic matter than the Barnfield and Broadbalk soil. This

suggests that for soils of the same texture and pH there is a range of change points controlled by other, as yet unidentified, factors.

Figure 2*b* shows CaCl<sub>2</sub>-P plotted against Olsen P for soils with pH < 5.8 and soils given (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> irrespective of their pH in 1992. The change point (120 mg Olsen P/kg) is twice that for soils with pH > 5.8 and is very similar to that (112 mg Olsen P/kg) for soils with pH < 5.8 but not receiving (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (McDowell & Condron 1999). The fact that all (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> treated soils, irrespective of whether the pH was above or below 5.8 in 1992 behaved as other soils with pH < 5.8 can be explained as follows. In 1856, the soil pH was 5.7–5.8 and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> acidified the soil further, to pH 3.9 by 1923 (Warren & Johnston 1964). The 4-yearly

Table 4. *Chemical characteristics, CaCl<sub>2</sub>-P and ion activity products (IAP;  $pAl^{3+} + pOH^- + pH_2PO_4^-$ ) for ammonium sulphate fertilized plots 4/2, 9/2 and 11/1 (soil samples 0–7.5 cm\*)*

Subplot	pH	Organic C (g/kg)	Olsen P (mg/kg)	CaCl <sub>2</sub> -P (mg/l)	IAP
4/2a	6.0	58	132	1.5	–28.3
4/2b	4.6	47	168	1.8	–30.4
4/2c	4.6	82	195	4.1	–29.6
9/2a	6.3	58	139	1.6	–28.5
9/2b	5.2	51	141	1.5	–29.4
9/2c	5.4	122	151	2.3	–29.9
11/1a	5.9	80	156	1.5	–28.3
11/1b	5.5	76	129	1.1	–30.3
11/1c	4.2	119	157	1.9	–31.4

\* Differences in organic C between *a/b* and *c* subplots reflect the fact that *a/b* subplots were limed from 1903 while *c* subplots were not limed until 1965. More organic carbon accumulated under the acidic conditions on the *c* subplots (Warren & Johnston 1964).

application of lime to half plots started in 1903 and this increased pH gradually to 4.1–4.8 by 1923 and 4.2–5.7 by 1959 (Warren & Johnston 1964). Increased amounts of lime, added after 1965 to raise the pH on subplots *a*, *b* and *c* to 7, 6 and 5, respectively, were applied over a number of years, and the pH increased only slowly. Thus, the soil P chemistry controlling the ratio of CaCl<sub>2</sub>-P to Olsen P was determined by the fact that these soils had a pH less than 5.8 for most of the 135 years (1856–1991).

#### *Data for soils from the laboratory experiment*

Results from the laboratory liming experiment showing the change in CaCl<sub>2</sub>-P and Olsen P as a result of adding lime to the six soils, three with and three without continual long-term application of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, none of which had ever received lime in the field experiment, are shown in Fig. 3. Figures 3a and 3b show the change in CaCl<sub>2</sub>-P and Olsen P, respectively, on the soils which have received (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> annually since 1856. Olsen P was least on plot 11/1d and most on plot 4/2d, reflecting the difference in P offtake over the history of the experiment. The 30-day period of incubation at different pHs had little consistent effect on either CaCl<sub>2</sub>-P or Olsen P. This supports the conclusion from the field experiment data in Fig. 2 and suggests that soil P chemistry relating CaCl<sub>2</sub>-P and Olsen P has been long established and is not changed by liming in the short term.

Figures 3c and 3d also show changes in CaCl<sub>2</sub>-P and Olsen P but for the three unlimed soils that had

never received (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Again, the concentrations of Olsen P reflect P balances on each of the three plots over the history of the experiment. The difference in behaviour between the soil from plot 13 and those from plots 15 and 16 can be explained in part by the previous treatments of these plots. Plot 13 received N as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> until 1904 – organic manures only since 1905 – and by 1923 the soil pH was 4.8 and this changed very little subsequently, 4.7 in 1959 and 4.6 in 1991. Thus, the soil P chemistry of the inorganic P fraction was largely controlled by this low pH. As on the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> treated soils in Fig. 3a, CaCl<sub>2</sub>-P showed no consistent pattern of change with increasing pH in the laboratory liming experiment. However, there was some increase in Olsen P as pH increased from 7 to 8.5, perhaps as a result of organically bound inorganic P being displaced from sites on the organic matter. On plots 15 and 16, plot 16 has always received N as NaNO<sub>3</sub> and P every year, while plot 15 had N only, as NaNO<sub>3</sub>, until 1875 and subsequently P without N. The pH in water in 1923 was 5.5 and 5.9 on plots 15 and 16 respectively and these had declined to 4.9 and 5.4 by 1959 with little subsequent decrease. It is assumed that Na was lost in drainage as the balancing cation rather than Ca, leaving Ca on the exchange complex. In both soils CaCl<sub>2</sub>-P and Olsen P increased as pH increased from 6.0 to 8.5 and the increase in Olsen P was parallel to that on plot 13 (Fig. 3d). We can offer no explanation for the decline in both CaCl<sub>2</sub>-P and Olsen P between pH 5.0 and 6.0. The subsequent increase in both CaCl<sub>2</sub>-P and Olsen P following liming in the laboratory is probably related to the fact that the soils never became extremely acid.

Data for CaCl<sub>2</sub>-P and Olsen P from the laboratory liming experiment can be related to data from the field experiment. Data for plots 4/2d, 9/2d, 11/1d (Fig. 3a and b) and 13d (Fig. 3c and d) fit well to the relationship for acid soils in Fig. 2b. This is because the soil P chemistry for all four soils is dominated by the fact that for much of their history these soils had a pH below 5. The short period of the laboratory experiment (30 days) did little to change this soil P chemistry. Although soils from plots 15 and 16 had pH in water of 4.7 and 5.3 respectively in 1991, these soils never became very acid for a prolonged period of time and so soil P chemistry is intermediate between that of the very acid soils and those whose pH was always above > 5.8. Thus, after soils were limed in the incubation experiment, Fig. 2a shows that the relationship between CaCl<sub>2</sub>-P and Olsen P for these 'laboratory-limed' soils was somewhat below that for soils whose pH had been above 5.8 for a long period of time.

Figure 2 shows that relative to Olsen P, acid soils contain much less CaCl<sub>2</sub>-P than do soils with pH > 5.8. This is probably related to the retention of P by Al and Fe in complexes from which the P cannot

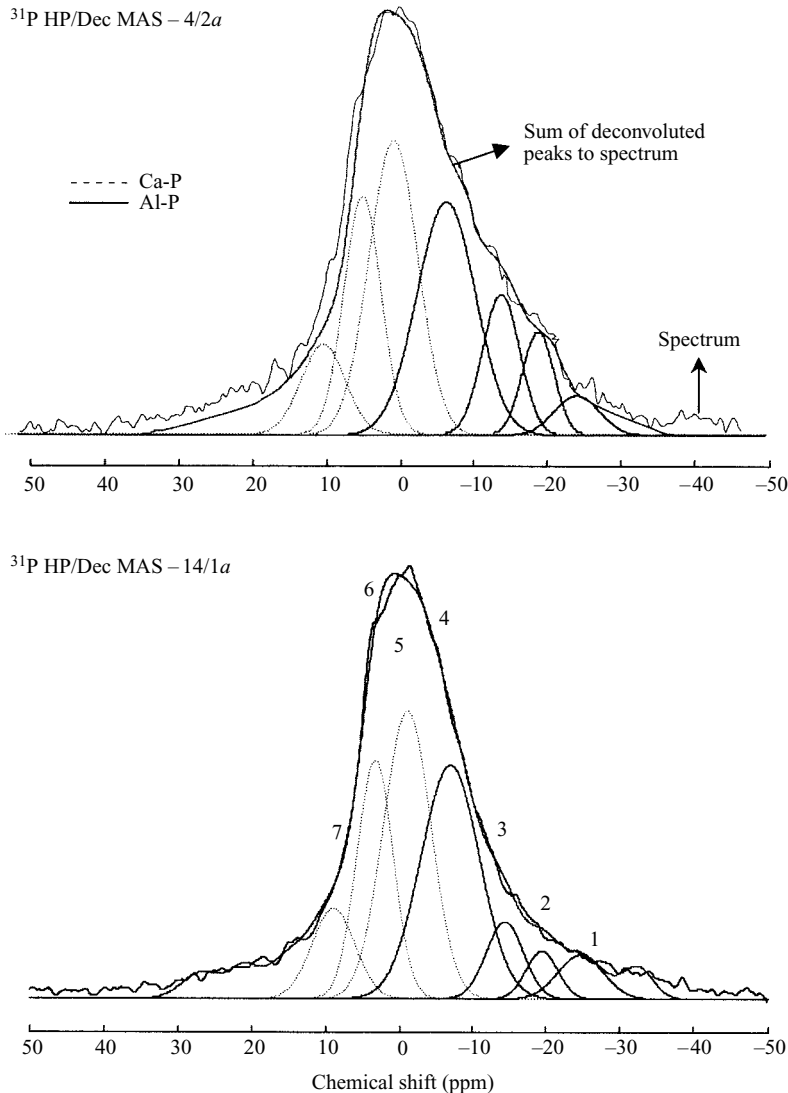


Fig. 4. Solid state  $^{31}\text{P}$  HP/Dec MAS NMR spectra for two soils of equivalent pH and total P concentration, one  $(\text{NH}_4)_2\text{SO}_4$  fertilized (4/2a) and the other not (14/1a). Numbers refer to assigned peaks from Table 1.

be extracted by 0.01 M  $\text{CaCl}_2$ , but can be extracted by Olsen's sodium bicarbonate reagent.

Coleman *et al.* (1960) demonstrated that Al-montmorillonite can react with P at  $\text{pH} < 7.0$  to form an amorphous solid,  $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4(\text{s})$ , following the hydrolysis of exchangeable  $\text{Al}(\text{III})$ . This solid phase was shown to have a solubility  $pK_{\text{so}}$  ( $= \text{pAl}^{3+} + \text{pOH}^- + \text{pH}_2\text{PO}_4^-$ ) of  $-27.8 \pm 0.1$ . Other P solubility studies with aluminosilicates or Al-bearing organic matter under acidic conditions, have suggested that the  $pK_{\text{so}}$  of these products falls between  $-27$  and  $-29$  (Veith & Sposito 1977; Bloom 1981). Previous work on Park Grass soils with  $\text{pH} < 5.8$  (excluding

$(\text{NH}_4)_2\text{SO}_4$  fertilized plots), showed that these soils are saturated and in equilibrium with respect to variscite ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $pK_{\text{so}} = -30.5$ ; Lindsay 1979) and its amorphous analogue respectively (McDowell 1999). The solubility of some Al-P minerals in 0.01 M  $\text{CaCl}_2$  was determined by comparing the ion activity product (IAP;  $\text{pAl}^{3+} + \text{pOH}^- + \text{pH}_2\text{PO}_4^-$ ) for  $(\text{NH}_4)_2\text{SO}_4$  fertilized soils that have received lime since 1963 with the  $pK_{\text{so}}$  values for variscite and its amorphous analogue (Table 4). These data show that  $(\text{NH}_4)_2\text{SO}_4$  fertilized plots are also saturated and/or near equilibrium with respect to variscite and its amorphous analogue. This suggests that over the 30-year period,

Table 5. Semi-quantitative concentrations of P species obtained by deconvolution of  $^{31}\text{P}$  HPDec/MAS NMR spectrum of a  $(\text{NH}_4)_2\text{SO}_4$  fertilized soil (11/1a,b) and non- $(\text{NH}_4)_2\text{SO}_4$  fertilized soil (14/1a,b) of equivalent pH and sum total of P determined by NMR method

Characteristic (mg/kg, except pH)	11/1a	11/1b	14/1a	14/1b
Variscite	45	75	49	44
Amorphous Al-P	351	315	230	166
Other Al-P	40	83	52	58
Fe-P	809	812	942	973
Ca-P	595	485	551	335
Sum total of P determined by NMR method	1840	1770	1824	1580
Olsen P	156	129	120	96
pH	5.9	5.5	6.0	5.6

the gradual application of lime has had little effect on P minerals formed under previously acidic conditions.

Aluminium solubility as a function of pH is at a minimum around pH 6 and increases with decreasing pH (Bache 1985). As noted previously, prior to 1903, the soil on  $(\text{NH}_4)_2\text{SO}_4$  fertilized *a* and *b* subplots and from 1965 the *c* subplots had a pH much less than 6. Therefore, soils receiving  $(\text{NH}_4)_2\text{SO}_4$  would have a greater amount of soluble Al than soils that did not receive  $(\text{NH}_4)_2\text{SO}_4$ . In a review of the effects of liming on P availability, Haynes (1982) concluded that the major effects of lime were to alleviate Al toxicity and increase P uptake by plants and precipitate Al. The highly active sorbing surfaces that formed could adsorb P and thereby decrease P availability. A comparison of solid state  $^{31}\text{P}$  HPDec/MAS NMR data for  $(\text{NH}_4)_2\text{SO}_4$  fertilized and non- $(\text{NH}_4)_2\text{SO}_4$  fertilized soils suggests this is reflected as amorphous Al-P in the spectra (Fig. 4). The soil receiving  $(\text{NH}_4)_2\text{SO}_4$  contained more than twice as much amorphous Al-P compared with the soil without  $(\text{NH}_4)_2\text{SO}_4$  (Table 5). The greater precipitation of Al and creation of active sorptive surfaces in  $(\text{NH}_4)_2\text{SO}_4$  fertilized soils compared with other soils, would decrease the amount of P that could be removed by 0.01 M  $\text{CaCl}_2$ . This effect was not reversed by liming previously acid soils in the laboratory incubation experiment.

Holford (1983) found that P soluble in 0.02 M KCl increased with pH from 4.8 to 5.8, probably due to the hydrolysis of Al- and Fe-P. When soils were limed above pH 6,  $\text{CaCl}_2$ -P and Olsen P began to increase. Previous work has shown that this can be attributed to a constant sorption capacity and a decrease in the soil's affinity to sorb P caused by the over-riding effect of increasing negative charge (Holford 1983). Our data basically support the Holford view which showed

a general increase in soluble P as pH increased from 4.8 to above pH 6.0 (Fig. 3).

Some work has shown a decrease in soluble P with increasing pH from 3 to 6 in soils high in exchangeable Al, and this effect has been attributed to the occlusion of P in precipitating hydrous oxides (Murrmann & Peech 1969; Amarasiri & Olsen 1973). However, if this was the dominant mechanism occurring in our soils, then amorphous Al-P detected by  $^{31}\text{P}$  HPDec/MAS NMR should be similar for soils which had the same pH before 1965, i.e. *a* and *b* subplots. Table 5 shows that the quantity of amorphous Al-P present in *a* and *b* subplots (both of similar total P concentration) was different. This suggests that P added annually as superphosphate since 1965 had been 'protected' to a different extent from reaction with active Al by the different amounts of  $\text{CaCO}_3$  added to increase soil pH.

## CONCLUSIONS

Data for both  $(\text{NH}_4)_2\text{SO}_4$  fertilized and non- $(\text{NH}_4)_2\text{SO}_4$  fertilized soils exhibit a change point in Olsen P above which  $\text{CaCl}_2$ -P increases much more per unit increase in Olsen P than if below this point. However, the change point is affected by pH and the nature of the soil's P sorbing system. For example, soils with pH 5.8 and above, exhibit a change point at about 60 mg Olsen P/kg, whereas soils below this pH exhibit a change point at about 120 mg Olsen P/kg. Soils fertilized annually with  $(\text{NH}_4)_2\text{SO}_4$  since 1856 exhibit a change point representative of soils with pH < 5.8 even though the pH of some of these soils has been raised above this pH since the 1970s. Thus, on these soils, soil P chemistry is still largely dominated by their history of being acid for many years and this soil P chemistry has little changed in soils where pH had been raised above 5.8 since the 1970s. Solubility and solid-state  $^{31}\text{P}$  MAS/Dec NMR data suggests that the smaller proportion of  $\text{CaCl}_2$ -P in acid soils is caused by the reaction of P with Al to form amorphous Al-P species.

When acid soils with different N fertilizer histories were limed in a laboratory incubation experiment to pHs ranging from 4 to 9, those that had not received  $(\text{NH}_4)_2\text{SO}_4$  and had not become very acid, had a change point similar to soils with a pH > 5.8. By contrast, those soils that had received  $(\text{NH}_4)_2\text{SO}_4$  and had an initial pH < 5.8 had a change point similar to soils with a pH < 5.8, irrespective of the pH to which they were raised in the liming experiment.

It is clear that in these soils of similar texture but different acidifying inputs over a long period of time, Al solubility has played a major role in determining P solubility and consequently P release to the soil solution and the potential for loss to surface waters. Although there was less potentially mobile P in soils with pH < 5.8, this pH is too acid for many arable crops grown in temperate climates.



This work was supported in part by grants from the Foundation for Research, Science and Technology (New Zealand, contract, AGRX0002), AGMART (New Zealand), St John's College (Cambridge University, Cambridge, UK) and grant AO 6462 from the UK Biotechnology and Biological Sciences Research

Council (BBSRC). The NMR instrumentation was provided by the University of London Intercollegiate Research scheme, and is located at University College, University of London, UK (Dr A. E. Aliev). IACR-Rothamsted receives grant-aided support from the BBSRC.

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